Relativistic and correlation effects on molecular properties - the interhalogens ClF, BrF, BrCl, IF, ICl and IBr

de Jong, W.A.; Styszynski, J.; Visscher, L.; Nieuwpoort, W.C.

published in
Journal of Chemical Physics
1998

DOI (link to publisher)
10.1063/1.476314

document version
Publisher's PDF, also known as Version of record

Relativistic and correlation effects on molecular properties: The interhalogens ClF, BrF, BrCl, IF, ICl, and IBr

W. A. de Jong
Laboratory for Chemical Physics and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

J. Styszynski
Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland

L. Visscher
Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark

W. C. Nieuwpoort
Laboratory for Chemical Physics and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 31 October 1997; accepted 23 December 1997)

The effect of relativity on the properties of the interhalogens ClF, BrF, BrCl, IF, IBr, and IBr is studied by comparing relativistic and nonrelativistic calculations. Bond lengths, harmonic frequencies, and dissociation energies show that the bond is weakened in the relativistic formalism. Relativity increases the electric dipole moment whereas the electric quadrupole moment and dipole polarizability display an irregular behavior. The relativistic contributions to the electric dipole and quadrupole moment of the iodine containing molecules are 10%–20% of the total value, whereas the contributions in the other molecules cannot be neglected. The value of the electric quadrupole moment is dominated by the relativistic contributions. © *1998 American Institute of Physics.* [S0021-9606(98)00213-X]

I. INTRODUCTION

In two previous papers,[1,2] hereafter called paper I and paper II, the influence of relativity and correlation effects on spectroscopic constants in the series X_2 and HX (with X=F, Cl, Br, I, At) were studied. The methods used were Hartree–Fock (HF), second-order Møller–Plesset perturbation theory (MP2), Configuration Interaction with Single and Double excitations (CISD), Coupled Cluster with Single and Double excitations (CCSD), and the latter method perturbatively corrected for the effect of triple excitations [CCSD(T)]. This gives a range of correlation treatments, from no electron correlation in the HF method to a fairly high level of correlation in the CCSD(T) method.

In this paper we complete the previous work with a study on the spectroscopic properties of the interhalogen series XY (with X=F, Cl, Br, I). The influence of relativity and correlation on the spectroscopic properties are investigated at the correlated levels MP2, CCSD, and CCSD(T). Hardly any previous theoretical work is available on the spectroscopic properties, but much theoretical work has been done on the electric dipole moments. In these calculations relativistic effects were disregarded or approximated neglecting the spin–orbit interaction. Here we study the relativistic effects on the electric dipole and quadrupole moments and the dipole polarizability within a fully relativistic framework. Correlation effects for these properties are estimated by means of CISD calculations.

II. COMPUTATIONAL DETAILS

All calculations on the spectroscopic properties are performed using the MOLFDIR program package.[3,4] The property integrals needed to calculate the expectation values of the electric properties are obtained from the HERMIT[5] part of the DIRAC[6] program. The dipole polarizibility is evaluated as a response property using the propagator method[7] within the Random Phase Approximation,[8] with an adapted version[9] of the relativistic coupled cluster code RELCCSD[10,11] in MOLFDIR. A Gaussian distribution is used to represent the spatial extent of the nucleus in both the relativistic and the nonrelativistic calculations (for the exponents see Table I of paper II). The speed of light is taken to be 137.035 989 5 a.u. Basis sets for the halogens are described in paper II and will be denoted by apVDZ and apVTZ.

In the MP2, CC, and CISD calculations the halogens are treated as seven valence electron atoms, correlating only the valence *s* and *p* electrons. In the correlated calculations of the spectroscopic properties the highest virtuals (with energies above ten atomic units) are left out. In the CISD calculations on the electric properties all virtuals are included.

All molecular calculations are performed using C_{4v} symmetry. The atomic calculations are carried out in O_h. To prevent spurious discrepancies between the nonrelativistic and relativistic dissociation energies, we calculate both the nonrelativistic and the relativistic atomic asymptotes in a basis of spinors optimized for the average energy of the $5p_{1/2})^2$ $5p_{3/2})^3$ configuration.

TABLE I. Properties of CIF calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	1.619	1.590	907	918	10.5	17.1
DC-HF	1.620	1.590	905	915	9.0	15.2
DC+G-HF		1.590		915		15.2
NR-MP2	1.676	1.637	780	809	57.3	68.1
DC-MP2	1.677	1.637	780	808	55.9	
66.4						
NR-CCSD	1.674	1.632	782	814	48.6	56.1
DC-CCSD	1.674	1.633	783	814	47.3	54.7
NR-CCSD(T)	1.685	1.645	751	781	52.3	61.1
DC-CCSD(T)	1.685	1.645	751	780	51.0	59.4
NR-HF (Ref. 27)	1.585		912			
NR-CISD+Q (Ref. 28)	1.653				49.6	
NR-CPF (Ref. 29)	1.636				55.3	
Experiment (Ref. 16)	1.628		786		66.3	

Spectroscopic constants are obtained by fitting the potential energy curves to a fourth order polynomial in the internuclear distance. The electric properties are calculated at the experimental bond length. The quadrupole moment is computed relative to the center of mass of the molecule (considered for this purpose as two spherical symmetric atoms, separated by the equilibrium bond distance) using the masses 18.998 40, 34.968 85, 78.918 34, and 126.904 48 a.u. from Ref. 12 for F, Cl, Br, and I, respectively.

We calculate the electric properties as an expectation value of the CISD wave function. Since the Hellmann–Feynman theorem is not fullfilled[13,14] in a CISD calculation, our results will differ from a more rigorous energy derivative formulation. Kucharski *et al.*[15] compared these two approaches and found only small differences for the dipole moment of IF calculated with the MBPT(4) method.

III. RESULTS AND DISCUSSION

The calculated spectroscopic properties for the six interhalogen molecules ClF, BrF, BrCl, IF, ICl, and IBr are presented in Table I–VI. In Table VIII–X the results of the electric property calculations for, respectively, the dipole moment, quadrupole moment, and static dipole polarizability, are given. In Table VII and XI the relativistic effects, defined as x (relativistic)-x (nonrelativistic), on these properties are summarized.

A. Spectroscopic properties

The dissociation energy (D_e) shows a relativistic decrease for all interhalogen molecules. This decrease, arising from the spin–orbit coupling in the valence p shell, is also seen in the homonuclear diatomic molecules (see paper I). In these molecules the molecular spin–orbit coupling is almost completely quenched for elements up to iodine, while the atomic asymptotes are lowered for each atom by one-third of the ^2P atomic ground state splitting. Assuming complete quenching in the present series of molecules gives an estimated SO effect (hereafter called ASO only and given in Table VII) on the D_e of one-third of the atomic spin–orbit splitting from both atoms.

Relativity destabilizes the molecular bond leading to a longer equilibrium bond length (r_e) and a decrease of the harmonic frequencies (ω_e). This destabilization can be understood by looking at the molecular orbital formation by the valence p orbitals. The six atomic valence p orbitals combine to antibonding and bonding or molecular spin orbitals,

TABLE II. Properties of BrF calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	1.744	1.716	772	777	14.3	20.1
DC-HF	1.746	1.718	765	771	9.9	14.9
DC+G-HF		1.719		771		15.0
NR-MP2	1.797	1.759	674	699	60.7	70.1
DC-MP2	1.799	1.762	668	693	57.0	66.3
NR-CCSD	1.793	1.754	679	705	52.1	59.1
DC-CCSD	1.795	1.757	673	699	48.3	54.5
NR-CCSD(T)	1.804	1.765	655	679	55.6	63.1
DC-CCSD(T)	1.806	1.769	649	673	51.8	59.1
NR-HF (Ref. 27)	1.719		770			
Experiment (Ref. 16)	1.759		671		64.7	

TABLE III. Properties of ClBr calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	2.157	2.129	466	487	18.0	26.1
DC-HF	2.157	2.130	463	483	13.4	21.1
DC+G-HF		2.131		483		21.2
NR-MP2	2.188	2.143	427	458	44.4	55.1
DC-MP2	2.189	2.144	424	455	40.3	50.9
NR-CCSD	2.202	2.156	413	446	39.9	48.1
DC-CCSD	2.203	2.157	410	443	35.8	43.2
NR-CCSD(T)	2.212	2.165	399	433	42.7	51.2
DC-CCSD(T)	2.213	2.166	395	429	38.6	46.9
NR-HF (Ref. 27)	2.137		482			
Experiment (Ref. 16)	2.136		444		52.1	

TABLE V. Properties of ICl calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	2.355	2.319	408	424	21.5	29.1
DC-HF	2.362	2.326	395	411	13.9	20.9
DC+G-HF		2.327		411		21.0
NR-MP2	2.384	2.330	379	405	46.1	56.1
DC-MP2	2.392	2.338	366	392	39.4	49.1
NR-CCSD	2.397	2.341	368	395	42.0	49.1
DC-CCSD	2.406	2.349	355	383	35.3	41.7
NR-CCSD(T)	2.406	2.349	358	385	44.5	52.3
DC-CCSD(T)	2.416	2.359	344	372	38.0	45.2
NR-HF (Ref. 27)	2.33		421			
RCI (Ref. 30)	2.53		327			
Experiment (Ref. 16)	2.321		384		50.2	

which can be labeled as $\sigma_{1/2}$, $\pi_{1/2}$, $\pi_{3/2}$, $\pi^*_{1/2}$, $\pi^*_{3/2}$, $\sigma^*_{1/2}$. Spin–orbit coupling lifts the degeneracy of the π orbitals introducing σ character in the $\pi_{1/2}$ and $\pi^*_{1/2}$. The weakening of the chemical bond is caused by the introduction of antibonding character from the unoccupied $\sigma^*_{1/2}$ into the bonding $\pi_{1/2}$ orbital.

The size of the relativistic effects is similar to that in the homonuclear diatomics in paper I. The magnitude of the Gaunt interaction correction for the interhalogens is small, which suggests that higher-order two-electron relativistic effects will be small as well.

We will now compare our results with experimental data after which a comparison will be made with the few available theoretical results. Our r_e are longer than the experimental values, varying from less then 0.01 Å for the lighter to 0.05 Å for the heaviest molecules. The errors in the ω_e are generally smaller than 10 cm^{-1}. The D_e values are systematically too low by 5 kcal/mol. However, for the iodine molecule we have shown[26] that extensive core–valence correlation and the addition of a g-type basis function reduces the r_e with around 0.04 Å and increases the ω_e and D_e with 10 cm^{-1} and 5.5 kcal/mol, respectively.

There are hardly any theoretical results available for the spectroscopic properties of the interhalogens. Straub and McLean[27] performed a systematic study on these molecules at the Hartree–Fock level within the nonrelativistic framework. Their findings are in close agreement with our nonrelativistic NR-HF results, except for IBr, where they had to use a basis set of lower quality due to the limited computational resources at the time.

For the ClF molecule we can compare our results with other theoretical work, the CISD+Q calculations of Pettersson *et al.*[28] and the CPF calculations of Scharf and Ahlrichs,[29] both in a nonrelativistic framework. The results in these papers agree very well with our nonrelativistic correlated work. Balasubramanian[30] calculated the ICl molecule using averaged relativistic effective potentials (AREP), followed by CI calculations to include spin–orbit effects. We find large discrepancies between his results and the ones presented here.

B. Electric properties

In contrast to the spectroscopic properties, much theoretical attention has been given to the electric properties, especially to the dipole moment μ_z. Most of the calculations are performed within a nonrelativistic framework, whereas in some calculations relativistic corrections are included either by the use of a Cowan–Griffin (CG)[31] or a Douglas–Kroll (DK)[32,33] Hamiltonian, both without spin–orbit coupling.

1. Dipole moment

The electric dipole moment (μ_z) presented in Table VIII, shows a relativistic increase for all molecules. We find

TABLE IV. Properties of IF calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	1.904	1.876	698	703	24.6	30.1
DC-HF	1.914	1.886	675	680	16.3	20.7
DC+G-HF		1.887		680		20.9
NR-MP2	1.954	1.916	622	645	69.2	78.1
DC-MP2	1.965	1.928	601	624	62.4	70.5
NR-CCSD	1.947	1.910	631	654	60.9	66.1
DC-CCSD	1.959	1.921	610	632	53.8	58.8
NR-CCSD(T)	1.956	1.920	613	634	64.1	70.5
DC-CCSD(T)	1.969	1.932	590	611	57.1	63.1
NR-HF (Ref. 27)	1.86		711			
Experiment (Ref. 16)	1.910		610		67.3	

TABLE VI. Properties of IBr calculated at various levels of theory.

	r_e (Å)		ω_e (cm^{-1})		D_e (kcal mol^{-1})	
Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	2.508	2.472	284	295	18.4	25.7
DC-HF	2.510	2.475	276	287	8.0	14.5
DC+G-HF		2.476		287		14.6
NR-MP2	2.537	2.483	264	283	40.2	50.5
DC-MP2	2.541	2.486	256	275	30.9	40.4
NR-CCSD	2.552	2.497	255	275	37.2	44.0
DC-CCSD	2.557	2.501	246	266	28.0	34.1
NR-CCSD(T)	2.562	2.506	247	267	39.5	47.1
DC-CCSD(T)	2.568	2.511	237	258	30.4	37.4
NR-HF (Ref. 27)	2.40		342			
Experiment (Ref. 16)	2.469		269		42.3	

TABLE VII. Relativistic effects on the spectroscopic properties at different levels of theory.

		Δr_e (Å)		$\Delta \omega_e$ (cm^{-1})		ΔD_e (kcal mol^{-1})	
Molecule	Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
ClF	HF	0.001	0.000	−2	−2	−1.5	−1.5
	HF+G		0.000		−3		−1.5
	MP2	0.000	0.001	0	−1	−1.3	−1.4
	CCSD	0.000	0.001	0	−1	−1.3	−1.4
	CCSD(T)	0.000	0.001	0	−1	−1.3	−1.4
	ASO only					−1.3	
BrF	HF	0.002	0.003	−7	−6	−4.3	−4.6
	HF+G		0.003		−6		−4.5
	MP2	0.002	0.003	−6	−6	−3.7	−4.0
	CCSD	0.002	0.003	−6	−6	−3.8	−4.1
	CCSD(T)	0.002	0.003	−6	−6	−3.7	−4.0
	ASO only					−4.0	
BrCl	HF	0.000	0.001	−3	−3	−4.6	−4.9
	HF+G		0.001		−4		−4.8
	MP2	0.001	0.001	−3	−3	−4.1	−4.5
	CCSD	0.001	0.001	−3	−4	−4.1	−4.4
	CCSD(T)	0.001	0.001	−4	−4	−4.0	−4.3
	ASO only					−4.5	
IF	HF	0.010	0.010	−23	−23	−8.3	−8.8
	HF+G		0.011		−23		−8.7
	MP2	0.012	0.011	−21	−21	−6.9	−7.4
	CCSD	0.011	0.011	−21	−21	−7.2	−7.6
	CCSD(T)	0.012	0.012	−23	−23	−7.0	−7.4
	ASO only					−7.8	
ICl	HF	0.008	0.007	−13	−13	−7.6	−8.2
	HF+G		0.008		−13		−8.1
	MP2	0.009	0.008	−13	−12	−6.6	−7.4
	CCSD	0.009	0.009	−13	−13	−6.6	−7.2
	CCSD(T)	0.010	0.010	−14	−13	−6.5	−7.1
	ASO only					−8.3	
IBr	HF	0.003	0.003	−8	−8	−10.5	−11.2
	HF+G		0.004		−8		−11.0
	MP2	0.004	0.004	−8	−8	−9.3	−10.1
	CCSD	0.005	0.004	−9	−8	−9.2	−9.8
	CCSD(T)	0.006	0.005	−10	−9	−9.1	−9.7
	ASO only					−11.0	

that the relativistic contribution becomes increasingly important when going to the heavier interhalogens. For the iodine containing molecules this contribution is 10%–20% of the total value. The increase of the electric dipole moment can be understood by considering that relativistic effects reduce the ionization potential especially for the heaviest atom in the molecule, which leads to a more ionic molecule.[34] Our relativistic correlated μ_z overestimates the experimental values by 0.020–0.044 a.u., which is an error of 5%–9%. Our relativistic results (DC-HF) for the ClF molecule are similar to those of Sadlej[35] and Perera and Bartlett.[36] However, for the other molecules significant differences are found and these differences increase for heavier molecules. The smaller relativistic corrections of Sadlej and Perera and Bartlett (Table XI) are probably due to the absence of a spin–orbit interaction in the Cowan–Griffin Hamiltonian. Fowler *et al.*[37] included relativistic effects in their calculations on the BrCl molecule using the one-component form of the Douglas–Kroll approximation. Here the spin–orbit coupling is also neglected and the resulting relativistic effects are comparable to those of Sadlej and Perera and Bartlett.

In contrast to the results obtained for the other molecules, there are large differences between the DZ and TZ results of μ_z for the iodine-containing molecules. This suggests that in comparison with the other atoms the basis sets for the iodine atom lacks the necessary flexibility to reproduce this property well. Our NR-HF results are in close agreement with those of Sadlej[35] and Perera and Bartlett.[36] For the three lightest molecules the results with the basis sets of Sadlej are comparable to our double zeta (DZ) results, whereas in the iodine-containing molecules they lie closer to the triple zeta (TZ) results. There are discrepancies between our results and those of Straub and McLean[27] and Kucharski *et al.*,[15] which are probably caused by basis set deficiencies in these calculations. Fowler *et al.*[37,38] performed calculations on the BrCl molecule and their nonrelativistic results are in close agreement with our data. Pettersson *et al.*[28] studied the ClF molecule, and their nonrelativistically calculated μ_z is significantly lower than our value and that of the other authors.

Our correlation contributions are smaller than those of Sadlej[35] and Kucharski *et al.*,[15] both using MBPT (4), and Perera and Bartlett,[36] using CCSD(T). Pettersson *et al.*[28] included correlation contributions using CISD for the ClF mol-

TABLE VIII. Calculated dipole moment μ_z (a.u.). The positive sign means polarity X^+Y^-.

	Molecule											
	ClF		BrF		BrCl		IF		ICl		IBr	
Method[a]	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	0.446	0.438	0.653	0.644	0.197	0.201	0.865	0.790	0.488	0.425	0.292	0.243
DC-HF	0.452	0.444	0.688	0.680	0.230	0.234	0.978	0.900	0.616	0.548	0.395	0.340
NR-SDCI	0.372	0.378	0.561	0.569	0.185	0.194	0.776	0.709	0.470	0.405	0.283	0.226
DC-SDCI	0.377	0.383	0.593	0.601	0.215	0.224	0.878	0.810	0.586	0.518	0.373	0.313
NR-HF (Ref. 27)	0.355		0.567		0.231		0.570				0.254	
NR-HF (Ref. 35)	0.446		0.652		0.205		0.814		0.442		0.258	
CG-HF (Ref. 35)	0.451		0.679		0.229		0.891		0.514		0.305	
CG-MBPT (4) (Ref. 35)	0.359		0.556		0.198		0.753		0.454		0.263	
NR-HF (Ref. 38)					0.206							
NR-HF (Ref. 15)	0.479		0.715		0.266		0.930		0.563		0.334	
NR-MBPT(4) (Ref. 15)	0.350		0.550		0.222		0.735		0.472		0.274	
NR-HF (Ref. 36)	0.446		0.658		0.204		0.813		0.442		0.257	
CG-HF (Ref. 36)	0.451		0.685		0.228		0.890		0.514		0.296	
CG-CCSD(T) (Ref. 36)	0.354		0.560		0.199		0.756		0.443		0.264	
NR-HF (Ref. 37)					0.196							
DK-HF (Ref. 37)					0.221							
DK-CCSD(T) (Ref. 37)					0.183							
NF-HF (Ref. 28)	0.409											
NR-CISD+Q (Ref. 28)	0.346											
NR-CPF (Ref. 29)	0.334											
Experiment	0.3494±0.0079 (Ref. 17) 0.346±0.008 (Ref. 18)		0.559±0.006 (Ref. 19)		0.204±0.002 (Ref. 20)		0.766±0.008 (Ref. 21)		0.49±0.01 (Ref. 22) 0.475±0.001 (Ref. 23)		0.290±0.004 (Ref. 24) 0.286±0.011 (Ref. 25)	

[a]CG (Cowan–Griffin Hamiltonian used to include relativistic effects); DK (Douglas–Kroll Hamiltonian used to include relativistic effects). DK (Douglas–Kroll Hamiltonian used to include relativistic effects).

TABLE IX. Calculated quadrupole moment Θ_{zz} (a.u.).

	Molecule											
	ClF		BrF		BrCl		IF		ICl		IBr	
Method[a]	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	0.901	0.828	0.514	0.382	3.043	2.515	0.250	0.059	3.026	2.313	4.611	3.696
DC-HF	0.911	0.836	0.483	0.349	3.058	2.533	−0.003	−0.189	2.803	2.123	4.657	3.772
NR-SDCI	0.977	0.912	0.706	0.557	2.974	2.535	0.443	0.255	2.926	2.352	4.485	3.722
DC-SDCI	0.987	0.922	0.688	0.534	2.998	2.560	0.235	0.045	2.749	2.196	4.568	3.815
NR-HF (Ref. 27)	0.950		0.503		2.617		0.639				3.361	
NR-HF (Ref. 35)	0.947		0.519		2.845		0.199		2.584		4.165	
CG-HF (Ref. 35)	0.958		0.514		2.883		0.124		2.597		4.361	
CG-MBPT(4) (Ref. 35)	1.102		0.833		2.875		0.483		2.635		4.272	
NR-HF (Ref. 38)[b]					2.797							
Experiment[c]	1.00±0.74		0.68±0.74									
	0.65±0.74		0.91±0.74									

[a]CG (Cowan–Griffin Hamiltonian used to include relativistic effects).
[b]A bond length of 2.141 Å is used.
[c]Reference 18. The first entries in the FCl and FBr column corresponds to the isotopes ^{35}Cl and ^{79}Br, whereas the second entries are the isotopes ^{37}Cl and ^{81}Br.

ecule, and their results are similar to our calculated correlation effects. It is clear that more extensive correlation calculations are required to get closer agreement with the experimental results.

2. Quadrupole moment

We find large relativistic effects for the IF and ICl molecule. In the case of the IF molecule the relativistic effects dominate the magnitude of the Θ_{zz} value and at the HF level of theory the sign is even reversed. The Θ_{zz} of the two lightest molecules, ClF and BrF are within the wide error bars of the experimental data. Our relativistic contributions to the Θ_{zz} differ considerably from those calculated by Sadlej[35] for all molecules, except the lightest, ClF. Sadlej found small relativistic effects for all molecules except for IBr, where our relativistic correction is only half of the correction calculated by Sadlej.

The Θ_{zz} shows basis set dependencies for all molecules, except for the two lightest molecules ClF and BrF. On the other hand, the relativistic effects do not seem to be basis set dependent. The NR-HF results of Sadlej[35] for the three lighter systems are comparable to our apVDZ results, whereas those for the iodine-containing molecules lie closer to the apVTZ results. This trend is similar to the one found for the μ_z. The results of Straub and McLean[27] for the first two molecules ClF and BrF are similar to our double zeta results, which is somewhat surprising because of the large discrepancies found for the dipole moments of these molecules. The BrCl and IBr results lie close to, or even below, the apVTZ values, whereas the results for the IF molecule show large deviations.

Not only the size but also the sign of the correlation corrections change when going from apVDZ to apVTZ quality basis sets. For the molecules BrCl, ICl and IBr, molecules with a large Θ_{zz}, the sign of the corrections changes from negative to positive, yielding a larger Θ_{zz} in the triple zeta calculation. The correlation contributions of Sadlej[35] do not show a systematic behavior either and differ from our corrections as well. More extensive correlated calculations and analysis of the correlation contributions are needed to get a better understanding of the correlation effects on this property.

3. Dipole polarizability

No experimental values are available for the α_{zz}. Significant relativistic effects are found for the four heaviest molecules BrCl, IF, ICl, and IBr, with the largest relativistic

TABLE X. Calculated dipole polarizability α_{zz} (a.u.).

	Molecule											
	ClF		BrF		BrCl		IF		ICl		IBr	
Method[a]	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
NR-HF	21.63	22.18	27.72	27.97	50.81	51.55	31.25	36.30	59.34	64.98	74.82	78.85
DC-HF	21.66	22.20	27.72	27.96	51.09	51.82	30.93	35.85	60.06	65.49	76.56	80.38
NR-HF (Ref. 35)	22.48		27.82		51.50		36.54		65.30		78.96	
CG-HF (Ref. 35)	22.51		27.80		51.65		36.07		65.30		79.24	
CG-MBPT(4) (Ref. 35)	22.71		27.44		50.92		37.79		65.26		77.96	
NR-HF (Ref. 37)					51.76							
DK-HF (Ref. 37)					51.89							
DK-CCSD(T) (Ref. 37)					51.23							

[a]CG (Cowan–Griffin Hamiltonian used to include relativistic effects); DK (Douglas–Kroll Hamiltonian used to include relativistic effects).

TABLE XI. Relativistic effects on electric properties.

		$\Delta\mu_z$ (a.u.)		$\Delta\Theta_{zz}$ (a.u.)		$\Delta\alpha_{zz}$ (a.u.)	
Molecule	Method	apVDZ	apVTZ	apVDZ	apVTZ	apVDZ	apVTZ
ClF	HF	0.006	0.006	0.010	0.009	0.03	0.02
	SDCI	0.005	0.005	0.011	0.010		
	HF (Ref. 35)	0.005		0.011		0.03	
	HF (Ref. 36)	0.004					
	CCSD (Ref. 36)	0.004					
BrF	HF	0.036	0.036	−0.031	−0.033	0.00	−0.01
	SDCI	0.032	0.032	−0.018	−0.023		
	HF (Ref. 25)	0.028		−0.005		−0.02	
	HF (Ref. 36)	0.027					
	CCSD (Ref. 36)	0.023					
BrCl	HF	0.033	0.033	0.015	0.018	0.29	0.27
	SDCI	0.031	0.030	0.024	0.025		
	HF (Ref. 35)	0.023		0.038		0.15	
	HF (Ref. 36)	0.023					
	CCSD (Ref. 36)	0.019					
	HF (Ref. 37)	0.025					0.13
	CCSD (Ref. 37)	0.019					
IF	HF	0.113	0.111	−0.253	−0.248	−0.32	−0.46
	SDCI	0.102	0.101	−0.208	−0.210		
	HF (Ref. 35)	0.077		−0.075		−0.47	
	HF (Ref. 36)	0.077					
	CCSD (Ref. 36)	0.065					
ICl	HF	0.127	0.123	−0.224	−0.191	0.71	0.51
	SDCI	0.116	0.112	−0.177	−0.156		
	HF (Ref. 35)	0.072		0.013		0.00	
	HF (Ref. 36)	0.072					
	CCSD (Ref. 36)	0.057					
IBr	HF	0.102	0.097	0.046	0.076	1.74	1.53
	SDCI	0.091	0.087	0.084	0.093		
	HF (Ref. 35)	0.047		0.196		0.28	
	HF (Ref. 36)	0.039					
	CCSD (Ref. 36)	0.033					

effects on IBr. Relativity leads to an increase of the α_{zz}, except for the IF molecule, where a significant decrease is found. Our relativistic effect on the α_{zz} of BrCl is larger than the values obtained by Sadlej[35] and Fowler *et al.*,[37] whereas the value of Sadlej for the IF molecule is in close agreement with our result. Large discrepancies in the relativistic effects are found for the heavier molecules ICl and IBr.

Our NR-HF results are in close agreement with the results of Sadlej[35] and Fowler *et al.*,[37] as can be seen in Table X. We have not performed correlated calculations. The results of Sadlej in Table X give small effects for most of the molecules.

C. Additivity

Our results for the spectroscopic properties r_e and ω_c in Table VII show that for all practical purposes the relativistic and the correlation effects in the studied interhalogens are additive contributions. Some small combined relativistic-correlation contributions are seen for the ΔD_e. We also find a small combined effect of relativity and correlation for the μ_z of the iodine-containing molecules. These effects are similar to those found by Perera and Bartlett.[35] The combined effect of relativity and correlation for the Θ_{zz} is somewhat larger than what we observe in calculations on the μ_z.

IV. CONCLUSIONS

The effect of relativity on the spectroscopic and electric properties of the interhalogens has been studied, comparing nonrelativistic with relativistic all-electron calculations. The effect of the Gaunt correction, the higher-order two-electron relativistic correction, is found to be negligible. The inclusion of relativity leads to a weakening of the bond, which results in an increase of the r_e and a decrease of the ω_e. This weaker bond is caused by an increase of the antibonding character of the occupied valence spin orbitals. The relativistic effect on the dissociation energy is primarily due to the lowering by spin–orbit splitting of the ^2P atomic asymptote.

Relativistic effects increase the electric dipole moment (μ_z) of the interhalogens. This effect is largest for the iodine-containing molecules, where an increase of 10%–20% is found. Similar relativistic corrections are found for the Θ_{zz}. The electron correlation contribution decreases the μ_z and is underestimated at the CISD level of theory. The relativistic effects on the electric quadrupole moment (Θ_{zz}) are important but do not show a clear trend. We find that the value of Θ_{zz} in IF is dominated by the relativistic contribution. Our DHF results for the Θ_{zz} are in close agreement with other theoretical predictions, but the correlation contri-

bution is not converged with the basis set size and shows an irregular behavior. Relativistic effects increase the dipole polarizability (α_{zz}), except for the IF molecule where a significant decrease is found. Our nonrelativistic results for the α_{zz} are in close agreement with the available theoretical results but considerable differences are found when relativistic effects are included in the calculation.

For all practical purposes the relativistic and correlation effects on the spectroscopic properties yield additive contributions for the molecules studied here. However, the calculations on the electric dipole and quadrupole moment show somewhat larger deviations from additivity.

ACKNOWLEDGMENTS

This work was sponsored by the Netherlands Foundation for Chemical Research (SON) and the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputer facilities, both with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO). JS gratefully acknowledges a partial support of this work by the REHE programme of the ESF. LV wishes to acknowledge support from the Training and Mobility of the Researchers programme (Contract No. ERBFMBICT960738) of the European Union.

[1] L. Visscher and K. G. Dyall, J. Chem. Phys. **104**, 9040 (1995).
[2] L. Visscher, J. Styszynski, and W. C. Nieuwpoort, J. Chem. Phys. **105**, 1987 (1995).
[3] MOLFDIR, P. J. C. Aerts, O. Visser, L. Visscher, H. Merenga, W. A. de Jong, and W. C. Nieuwpoort, University of Groningen, The Netherlands, 1995.
[4] L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwpoort, Comput. Phys. Commun. **81**, 120 (1994).
[5] HERMIT. A molecular integral program, T. Helgaker, P. R. Taylor, and K. Ruud.
[6] DIRAC. Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations, T. Saue.
[7] J. Oddershede, P. Jørgensen, and D. L. Yeager, Comput. Phys. Rep. **2**, 33 (1984).
[8] G. Aucar and J. Oddershede, Int. J. Quantum Chem. **47**, 425 (1993).
[9] L. Visscher, T. Saue, and J. Oddershede, Chem. Phys. Lett. **274**, 181 (1996).
[10] L. Visscher, K. G. Dyall, and T. J. Lee, J. Chem. Phys. **105**, 8769 (1996).
[11] RELCCSD, L. Visscher, T. J. Lee, and K. G. Dyall, NASA Ames Research Center, Moffett Field, CA, 1995.
[12] A. H. Wapstra and K. Bos, At. Data Nucl. Data Tables **19**, 177 (1977).
[13] G. H. F. Diercksen, W. P. Kramer, and A. J. Sadlej, Chem. Phys. Lett. **82**, 117 (1981).
[14] V. Kellö and A. J. Sadlej, J. Chem. Phys. **93**, 8122 (1990).
[15] S. A. Kucharski, J. Noga, and R. J. Bartlett, J. Chem. Phys. **88**, 1035 (1988).
[16] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[17] R. E. Davis and J. S. Muenter, J. Chem. Phys. **57**, 2836 (1972).
[18] J. J. Ewing, H. L. Tigelaar, and W. H. Flygare, J. Chem. Phys. **56**, 1957 (1972).
[19] K. P. R. Nair, J. Hoeft, and E. Tiemann, J. Mol. Spectrosc. **78**, 506 (1979).
[20] K. P. R. Nair, J. Hoeft, and E. Tiemann, Chem. Phys. Lett. **58**, 153 (1978).
[21] K. P. R. Nair, J. Hoeft, and E. Tiemann, Chem. Phys. Lett. **60**, 253 (1979).
[22] E. Herbst and W. Steinmetz, J. Chem. Phys. **56**, 5342 (1972).
[23] A. Durand, J. C. Loison, and J. Vigué, J. Chem. Phys. **106**, 477 (1997).
[24] E. Tiemann and A. Dreyer, Chem. Phys. **23**, 231 (1977).
[25] K. P. R. Nair and J. Hoeft, J. Mol. Struct. **79**, 227 (1982).
[26] W. A. de Jong, L. Visscher, and W. C. Nieuwpoort, J. Chem. Phys. **107**, 9046 (1997).
[27] P. A. Straub and A. D. McLean, Theor. Chim. Acta **32**, 226 (1974).
[28] L. G. M. Pettersson, P. E. M. Siegbahn, and O. Gropen, Mol. Phys. **48**, 871 (1983).
[29] P. Scharf and R. Ahlrichs, Chem. Phys. **100**, 237 (1985).
[30] K. Balasubramanian, Chem. Phys. **95**, 225 (1985).
[31] R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976).
[32] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).
[33] B. A. Heß, Phys. Rev. A **33**, 3742 (1986).
[34] Numerical atomic calculations give a relativistic decrease of the ionization potential of F: 0.02 eV; Cl: 0.03 eV; Br: 0.09 eV; and I: 0.21 eV.
[35] A. J. Sadlej, J. Chem. Phys. **96**, 2048 (1992).
[36] S. A. Perera and R. J. Bartlett, Chem. Phys. Lett. **216**, 606 (1993).
[37] P. W. Fowler, S. A. Peebles, A. C. Legon, and A. J. Sadlej, Chem. Phys. Lett. **257**, 249 (1996).
[38] P. W. Fowler, A. C. Legon, S. A. Peebles, and E. Steiner, Chem. Phys. Lett. **238**, 163 (1995).